

SINGLE-COMPONENT POLYORGANOSILOXANE (POS) COMPOSITIONS
WHICH CROSSLINK TO FORM ELASTOMERS BY MEANS OF
POLYCONDENSATION REACTIONS AT AMBIENT TEMPERATURE AND
IN THE PRESENCE OF WATER, AND ELASTOMERS THUS OBTAINED

5

The field of the invention is that of single-component silicone mastics which are stable on storage in the absence of moisture and which crosslink by polycondensation reactions catalyzed using a mixed
10 titanium/metal catalyst to give nonyellowing elastomers which adhere to various supports, the reactions being carried out at ambient temperature (for example, 5 to 35°C) and in the presence of water (for example, ambient moisture).

15 Such mastics based on silicone elastomers are used in numerous applications, in particular in the construction industry, as means for rendering leaktight, for pointing, for coating and/or for assembling, inter alia. The rheological properties of
20 these single-component silicone mastics (pasty form) form the subject of much attention in these applications. It is the same as regards their resistance to bad weather and to heat, their flexibility at low temperature, their ease of use and
25 their rapid crosslinking/curing in situ on contact with atmospheric moisture.

The polycondensation reactions referred to above are those where Si-OR^0 bonds react with one another (the substituent R^0 can, for example, be an alkyl, acyl
30 or imino residue) in the presence of water. In the case where R^0 is, for example, an alkyl residue, the polycondensation reactions in question then give off an alcohol R^0OH . Generally, the kinetics of the polycondensation reactions are extremely slow; these
35 reactions are thus catalyzed by an appropriate catalyst.

Recourse is generally had, as catalysts which are used, to catalysts based on tin, on titanium or on an amine or compositions of these catalysts. The catalysts

based on tin (cf. in particular FR-A-2 557 582) and on titanium (cf. in particular FR-A-2 786 497) are catalysts having a satisfactory effectiveness. Other catalysts are sometimes mentioned, such as catalysts
5 based on zinc, on zirconium or on aluminum, but they have only been used to a slight extent industrially because of their mediocre effectiveness.

Tin-based catalysts are widely employed but their use sometimes suffers from the marked toxicity of tin
10 and it is important, for this reason, to find other catalysts which are as effective but less toxic. Titanium-based catalysts, which are also widely employed, exhibit two major disadvantages, however: they have slower kinetics than tin-based catalysts and,
15 in the case of the preparation of neutral single-component silicone compositions (where R^0 is an alkyl or imino residue), elastomers are obtained which retain a tacky surface feel several hours after having a skin and, during this time, they remain sensitive to the
20 capture of dust, for example. It should be added to this that the mastics catalyzed by tin frequently exhibit problems of stability, in particular when they give off an alcohol, which is not generally the case when the catalyst is a titanium-based compound.

25 It is known that mixed titanium/tin catalysis (cf. in particular SU-A-1 594 195) makes it possible to improve the performance of catalysis with titanium but once again the presence of tin is encountered.

It has now been found, and it is this which
30 constitutes the essential object targeted by the present invention, that it is possible:

- first, to substantially accelerate the setting kinetics related to the use of titanium-based catalysts by introducing, into the
35 crosslinkable single-component POS composition, a mixed catalyst consisting of the combination of a titanium-based compound with a specific metal compound in which the metal is other than tin; and

- secondly, to achieve surface crosslinking kinetics which, to say the least, are very close to those provided by the tin-based catalyst used alone;
- 5 - finally, to use only a small amount of titanium-based compound (which is known to sometimes bring about yellowing of the compositions) by combining it with a specific metal compound which will be completely colorless, which then makes it possible to greatly reduce the level of yellowing possible for the mastic, this measure being particularly advantageous in the case where it is desired to have available translucent mastics.

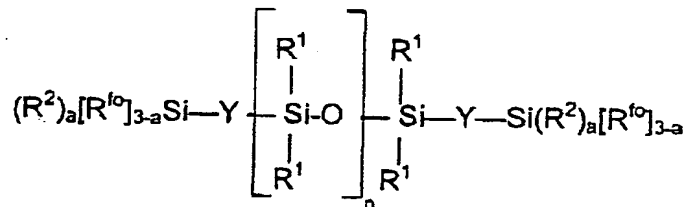
15 The advantages attached to the use of the present invention are thus summarized as follows:

- kinetics very similar to those of the tin-based catalyst are encountered;
- the tacky feel of the surface of the elastomer in the first days following crosslinking is reduced or eliminated;
- 20 - no tin is introduced;
- the ability of the mastic to turn yellow can be reduced by lowering the level of titanium.

25 It has also been demonstrated that: the abovementioned advantages are still obtained when, in the combination mentioned above, the titanium-based compound is replaced by a zirconium-based compound; there exists a marked synergistic effect between the two metal compounds used in combination in accordance with the content of the present invention.

35 More specifically, the present invention relates, in its first subject matter, to a single-component polyorganosiloxane composition (POS) which is stable on storage in the absence of moisture and which crosslinks in the presence of water to give a nonyellowing and adherent elastomer, said composition comprising:

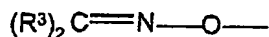
(i) at least one crosslinkable linear polyorgano-polysiloxane **A** of formula:



(I)

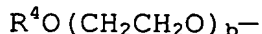
in which:

- the substituents R^1 , which are identical or different, each represent a saturated or unsaturated, substituted or unsubstituted, aliphatic, cyclanic or aromatic, C_1 to C_{13} monovalent hydrocarbon radical;
- the substituents R^2 , which are identical or different, each represent a saturated or unsaturated, substituted or unsubstituted, aliphatic, cyclanic or aromatic, C_1 to C_{13} monovalent hydrocarbon radical;
- the functionalization substituents R^{fo} , which are identical or different, each represent:
 - an iminoxy residue of formula:



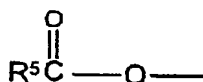
with R^3 independently representing a linear or branched C_1 to C_8 alkyl, a C_3 to C_8 cycloalkyl or a C_2 - C_8 alkenyl;

- an alkoxy residue of formula:



with R^4 independently representing a linear or branched C_1 to C_8 alkyl or a C_3 to C_8 cycloalkyl and $b = 0$ or 1 ;

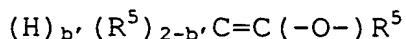
- an acyloxy residue of formula:



with R^5 representing a saturated or

unsaturated, substituted or unsubstituted, aliphatic, cyclanic or aromatic, C₁ to C₁₃ monovalent hydrocarbon radical;

- 5 • an enoxy residue of formula:

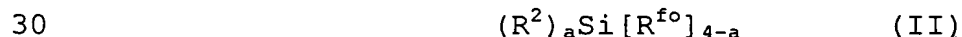


where R^5 is as defined above and $b' = 0, 1$ or $2i$

- 10
- each symbol Y represents an oxygen atom or a divalent hydrocarbon group;
 - n has a value sufficient to confer, on the POS **A**, a dynamic viscosity at 25°C ranging from 1000 to 1 000 000 mPa·s;
 - a is zero or 1;

(2i) optionally at least one polyorganosiloxane resin **B** functionalized by at least one radical R^{fo} corresponding to the definition given above and exhibiting, in its structure, at least two different siloxyl units chosen from those of formulae $(R^1)_3SiO_{1/2}$ (M unit), $(R^1)_2SiO_{2/2}$ (D unit), $R^1SiO_{3/2}$ (T unit) and SiO_2 (Q unit), at least one of these units being a T or Q unit, the radicals R^1 , which are identical or different, having the meanings given above with respect to the formula (I), said resin having a content by weight of functional radicals R^{fo} ranging from 0.1 to 10%, it being understood that a portion of the radicals R^1 are radicals R^{fo} ;

(3i) optionally at least one crosslinking agent **C** of formula:



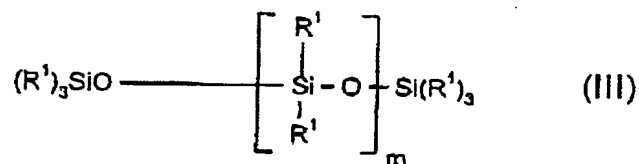
with R^2 , R^{fo} and a being as defined above;

(4i) optionally a residual amount of the functionalization catalyst **D** in the presence of which the preparation of the POS(s) **A** and of the optional
35 resin(s) **B** which are functionalized by R^{fo} takes place;

(5i) optionally at least one primary aliphatic C₁ to C₃ alcohol **E**;

(6i) optionally at least one unreactive linear

polydiorganosiloxane **F** which is not functionalized by R^{fo} and which has the formula:



in which:

- 5 - the substituents R^1 , which are identical or different, have the same meanings as those given above for the polyorganosiloxane **A** of formula (I);
- m has a value sufficient to confer, on the polymer of formula (III), a dynamic viscosity at 25°C ranging from
- 10 10 to 200 000 mPa·s;
- (7i) at least one inorganic filler **G**;
- (8i) optionally at least one auxiliary agent **H** known to a person skilled in the art which is generally chosen, when it is needed, according to the
- 15 applications in which the compositions according to the present invention are employed;
- (9i) an effective amount of a crosslinking/curing catalyst **I**; said composition being characterized by the following points (α), (β) and (γ):
- 20 • (α) the curing catalyst **I** consists of the combination of at least one organic derivative **I1** of a metal M1 chosen from titanium, zirconium and their mixtures with at least one organic derivative **I2** of a metal
- 25 M2 chosen from zinc, aluminum, boron, bismuth and their mixtures;
- (β) the number of $\mu g.at$ (microgram atoms) of the metals M1 + M2 introduced into 1 g of single-component composition comprising all the ingredients (i) to (8i) lies within the
- 30 range extending from 1 to 150 and preferably extending from 6 to 90;
- (γ) the ratio:

$$\frac{\text{number of } \mu g.at \text{ of M2}}{\text{total number of } \mu g.at \text{ of M1 + M2}} \times 100$$

lies within the range extending from 5 to 95% and preferably extending from 8 to 92%.

The single-component silicone mastic composition according to the invention has all the advantageous and specific properties of this type of product and exhibits, in addition, the following advantages, already mentioned above:

- kinetics very similar to those of the tin-based catalyst are encountered;
- 10 - the tacky feel of the surface of the elastomer in the first days following crosslinking is reduced or eliminated;
- no tin is introduced;
- the ability of the mastic to turn yellow can be reduced by lowering the level of metal M1.

15 In addition, the mastic composition according to the invention is economical and results in crosslinked elastomers possessing advantageous mechanical properties which adhere to numerous substrates, without even the presence of an adhesion promoter or auxiliary being absolutely essential.

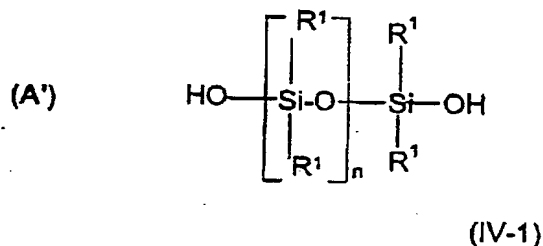
The composition according to the invention corresponds to an embodiment in which the essential constituent, namely the POS **A**, is at least partially functionalized at its ends by the following methods:

- 25 - when Y represents an oxygen atom: carrying out a condensation reaction between the end $\equiv\text{Si-OH}$ units of a precursor α,ω -hydroxylated POS **A'** and a functional group R^{fo} of a silane carrying functional groups R^{fo} ;
- 30 and
- when Y represents a divalent hydrocarbon group: carrying out an addition reaction between the end $\equiv\text{Si-H}$ units of a precursor α,ω -hydro POS **A''** and an olefinic silane carrying functional groups R^{fo} ; or alternatively
- 35 an addition reaction between the unsaturated ends (for example, vinyl or allyl) of a POS **A'''** and a hydrosilane carrying functional groups R^{fo} .

The POS **A** is functionalized according to techniques known to a person skilled in the art. This

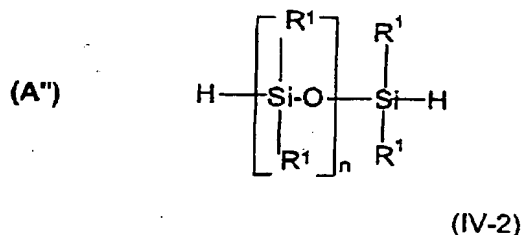
functionalized POS **A** corresponds to a stable form, in the absence of moisture, of the single-component mastic considered here. In practice, this stable form is that of the composition packaged in hermetically sealed cartridges which will be opened by the operator during use and which will allow him to apply the mastic over all the supports desired.

The hydroxylated precursor **A'** of the POS **A** functionalized by R^{fo} at the chain ends is an α, ω -hydroxylated polydiorganosiloxane of formula:



with R^1 and n being as defined above in the formula (I).

The hydro precursor **A''** of the POS **A** functionalized by R^{fo} at the chain ends is an α, ω -hydro polydiorganosiloxane of formula:



with R^1 and n being as defined above in the formula (I).

The precursor **A'''** of the POS **A** functionalized by R^{fo} at the chain ends is a polydiorganosiloxane corresponding to the definition given above for **A''**, except that the end hydrogen atoms are replaced by unsaturated groups.

The optional resin POS **B** functionalized by R^{fo} is produced in the same way as the POS **A** functionalized by R^{fo} , by condensation with the crosslinking silicone **C** carrying functionalization radicals R^{fo} . The precursor

of the resin POS **B** functionalized by R^{fo} is then a hydroxylated resin POS **B'** corresponding to the definition given above for **B**, except that a portion of the radicals R^1 correspond to OH groups.

5 The resin POS **B** functionalized by R^{fo} can also be produced by reaction of a precursor resin POS **B''** carrying $\equiv Si-H$ units with an olefinic silane carrying functional groups R^{fo} . This resin corresponds to the definition given above for **B**, except that a portion of
10 the radicals R^1 are now hydrogen atoms.

 The single-component mastic composition according to the invention can be of the acid type (in this case, the functionalization R^{fo} represents an acyloxy residue) or alternatively of the neutral type (in this case, the
15 functionalization R^{fo} represents an alkoxy or iminoxy or enoxy residue).

 It should be noted that at least a part of the inventive nature of the mastic according to the invention is due to the judicious and advantageous
20 selection of the combinations defined for metal compounds **I1** and **I2** used as curing catalyst **I**.

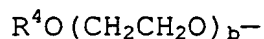
 According to a preferred embodiment of the invention, the single-component silicone composition concerned on the one hand comprises, as POS **A**, a
25 polymer of formula (I) in which the symbol Y represents an oxygen atom and, on the other hand, is of a neutral type according to which the functionalization substituents R^{fo} of the ingredients **A**, **B** and **C**, which are identical or different, each represent:

30 • an iminoxy residue of formula:



 with R^3 independently representing a linear or branched C_1 to C_8 alkyl, a C_3 to C_8 cycloalkyl or a C_2 - C_8 alkenyl, preferably
35 selected from the group consisting of methyl, ethyl, propyl, butyl, vinyl and allyl;

 • and/or an alkoxy residue of formula:



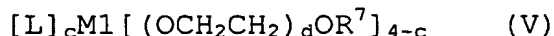
with R^4 independently representing a linear or branched C_1 to C_8 alkyl or a C_1 to C_8 cycloalkyl, preferably selected from the group consisting of methyl, ethyl, propyl, butyl and methyl glycol, and $b = 0$ or 1 .

This is because it could be observed that the problems of stability in the cartridge and of yellowing are more acute in the case where the mastics concerned are neutral single-component silicone mastics of iminoxy or alkoxy type.

According to a more preferred embodiment of the invention:

- the POS **A** is a polymer of formula (I) in which the symbol Y represents an oxygen atom;
- the functionalization substituents R^{fo} are of alkoxy type and correspond to the formula $R^4O(CH_2CH_2O)_b-$ as defined above; and
- the crosslinking/curing catalyst **I** consists of a combination:

- of at least one organic derivative **I1** of a metal M1 chosen from the group consisting of:
 - + monomers **I1.1** of formula:



in which:

- the symbol L represents a σ donor ligand, with or without π participation, such as, for example, the ligands of the type of those derived from acetylacetone, from β -keto esters, from malonic esters and from acetylimines;
- c represents 0, 1, 2, 3 or 4;
- M1 is a metal chosen from titanium, zirconium and their mixtures;
- the substituents R^7 , which are identical or different, each represent a linear or branched C_1 to C_{12} alkyl

radical;

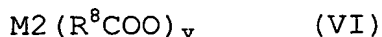
- d represents zero, 1 or 2;

- with the conditions according to which, when the symbol d represents zero, the alkyl radical R^7 has from 2 to 12 carbon atoms and, when the symbol d represents 1 or 2, the alkyl radical R^7 has from 1 to 4 carbon atoms;

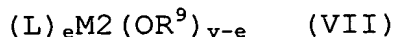
+ polymers **I1.2** resulting from the partial hydrolysis of the monomers of formula (V) in which the symbol c is at most equal to 3 and the symbol R^7 has the abovementioned meaning with the symbol d representing zero; with

• at least one organic derivative **I2** of a metal M2 chosen from the group consisting of:

+ the polycarboxylates **I2.1** of formula:



+ the metal alkoxides and/or chelates **I2.2** of formula:



+ in which formulae:

- the substituents R^8 , which are identical or different, each represent a linear or branched C_1 to C_{20} alkyl radical;

- the symbol R^9 has the meaning given above in the formula (V) for R^7 ;

- the symbol L represents a σ donor ligand, with or without π participation, such as, for example, the ligands of the type of those derived from acetylacetone, from β -keto esters, from malonic esters and from acetylmines;

- M2 is a metal of valency v chosen

from zinc, aluminum, bismuth, boron
and their mixtures;

- e represents a number ranging from
zero to v.

5 Without this being limiting, it should be
considered that the choices:

- as metal M1: of titanium, and
- as metal M2: of zinc, of aluminum or of their
mixtures,

10 are particularly appropriate choices in carrying out
the present invention.

 The use of these curing catalysts **I** in the
compositions according to the invention makes it
possible to obtain particularly surprising and
15 unexpected results marked by a synergy as regards in
particular skin formation time and hardness, in
comparison with what occurs when the metal compounds **I1**
and **I2** taken separately are used.

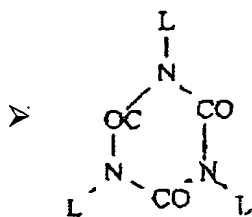
 The single-component organopolysiloxane
20 compositions according to the present invention can
additionally comprise one or more auxiliary agent(s) **H**,
such as in particular, per 100 parts by weight of
linear diorganopolysiloxane polymer(s) **A**:

- optionally from 0.1 to 10 parts of an adhesion
25 agent **H1**,
- optionally an effective amount of at least one
compound taken from the group formed by: anti-
fungals **H2**; bactericides **H3**; inert organic diluents
H4 (such as, in particular: petroleum fractions of
30 high boiling point, toluene, xylene, heptane, white
spirit, trichloroethylene or tetrachloroethylene);
plasticizers **H5** belonging, for example, to the group
of the alkylbenzenes with a molecular weight of
greater than 200 g/mol comprising a branched or
35 unbranched alkyl residue having from 10 to 30 carbon
atoms; thixotropic agents **H6**; stabilizing agents **H7**
(such as, in particular: an iron or cerium organic
acid salt, for example iron or cerium octoate; a
cerium oxide, a cerium hydroxide, an iron oxide, the

oxide CaO or the oxide MgO); or colored pigments **H8**.

Preferably, the adhesion agent **H1**, when one of them is used, is chosen from organosilicon compounds carrying both (1) hydrolyzable groups bonded to the silicon atom and (2) organic groups substituted by radicals chosen from the group of the isocyanato, epoxy, alkenyl, isocyanurate and (meth)acrylate radicals.

Mention may be made, by way of illustration of adhesion agents **H1**, of the organosilicon compounds defined below:



where L = $-(\text{CH}_2)_3-\text{Si}(\text{OCH}_3)_3$,

- (3-glycidoxypropyl)trimethoxysilane (GLYMO),
- vinyltrimethoxysilane (VTMS),
- methacryloyloxypropyltrimethoxysilane (MEMO),
- and their mixtures.

In order to explain in somewhat more detail the nature of the constituent components of the composition according to the invention, it is important to specify that the substituents R^1 of the polymers **POS A** functionalized by R^{fo} , of the resins **B** functionalized by R^{fo} and of the optional nonfunctionalized polymers **F** are selected from the group formed by:

- alkyl and haloalkyl radicals having from 1 to 13 carbon atoms,
- cycloalkyl and halocycloalkyl radicals having from 5 to 13 carbon atoms,
- alkenyl radicals having from 2 to 8 carbon atoms,
- mononuclear aryl and haloaryl radicals having from 6 to 13 carbon atoms,
- cyanoalkyl radicals, the alkyl members of which have from 2 to 3 carbon atoms,
- the methyl, ethyl, propyl, isopropyl, n-hexyl,

phenyl, vinyl and 3,3,3-trifluoropropyl radicals being particularly preferred.

More specifically still, and without implied limitation, the substituents R^1 mentioned above for the polymers POS **A** and **F** (optional) comprise:

- alkyl and haloalkyl radicals having from 1 to 13 carbon atoms, such as the methyl, ethyl, propyl, isopropyl, butyl, pentyl, hexyl, 2-ethylhexyl, octyl, decyl, 3,3,3-trifluoropropyl, 4,4,4-trifluorobutyl or 4,4,4,3,3-pentafluorobutyl radicals,
- cycloalkyl and halocycloalkyl radicals having from 5 to 13 carbon atoms, such as the cyclopentyl, cyclohexyl, methylcyclohexyl, propylcyclohexyl, 2,3-difluorocyclobutyl or 3,4-difluoro-5-methylcycloheptyl radicals,
- alkenyl radicals having from 2 to 8 carbon atoms, such as the vinyl, allyl or buten-2-yl radicals,
- mononuclear aryl and haloaryl radicals having from 6 to 13 carbon atoms, such as the phenyl, tolyl, xylyl, chlorophenyl, dichlorophenyl or trichlorophenyl radicals,
- cyanoalkyl radicals, the alkyl members of which have from 2 to 3 carbon atoms, such as the β -cyanoethyl and γ -cyanopropyl radicals.

Mention may be made, as concrete examples of siloxyl units D, $(R^1)_2SiO_{2/2}$, present in the diorganopolysiloxanes **A** functionalized by R^{fo} of formula (I), in the precursors **A'** and **A''** of formula (IV) and in the optional unreacted diorganopolysiloxanes **F** of formula (III), of:

- $(CH_3)_2SiO$,
- $CH_3(CH_2=CH)SiO$,
- $CH_3(C_6H_5)SiO$,
- $(C_6H_5)_2SiO$,
- $CF_3CH_2CH_2(CH_3)SiO$,
- $NC-CH_2CH_2(CH_3)SiO$,
- $NC-CH(CH_3)CH_2(CH_2=CH)SiO$,
- $NC-CH_2CH_2CH_2(C_6H_5)SiO$.

It should be understood that, in the context of

the present invention, use may be made, as precursor polymers **A'** and **A''** of formula (IV), of a mixture composed of several polymers which differ from one another in the value of the viscosity and/or the nature of the substituents bonded to the silicon atoms. Moreover, it should be indicated that the polymers **A'** and **A''** of formula (IV) can optionally comprise siloxyl units **T** of formula $R^1SiO_{3/2}$ and/or siloxyl units **Q**, $SiO_{4/2}$, in the proportion of at most 1% (this % expressing the number of **T** and/or **Q** units per 100 silicon atoms). The same comments apply to the unreactive polymers **F** (optional) of formula (III).

The substituents R^1 of the functionalized polymers **A**, of the precursor polymers **A'** and **A''** and of the unreactive and nonfunctionalized polymers **F** (optional) advantageously used, because of their availability in industrial products, are the methyl, ethyl, propyl, isopropyl, n-hexyl, phenyl, vinyl and 3,3,3-trifluoropropyl radicals. More advantageously, at least 80% by number of these substituents are methyl radicals.

Use is made of precursor polymers **A'** and **A''** having a dynamic viscosity at 25°C ranging from 1000 to 1 000 000 mPa.s and preferably ranging from 10 000 to 200 000 mPa.s.

As regards the nonfunctionalized polymers **F** (optional), they exhibit a dynamic viscosity at 25°C ranging from 10 to 200 000 mPa.s and preferably ranging from 50 to 150 000 mPa.s.

The unreactive and nonfunctionalized polymers **F**, when they are used, can be introduced all at once or in several fractions and at several stages or at a single stage of the preparation of the composition. The optional fractions can be identical or different in terms of nature and/or of proportions. Preferably, **F** is introduced all at once at a single stage.

Mention may be made, as examples of substituents R^1 of the resins **POS B** functionalized by R^{fo} which are suitable or which are advantageously used, of the

various radicals R^1 of the type of those mentioned by name above for the functionalized polymers **A**, the precursor polymers **A'** and **A''** and the unreactive and nonfunctionalized polymers **F** (optional). These silicone
5 resins are well known branched polyorganosiloxane polymers, the processes for the preparation of which are described in numerous patents. Mention may be made, as concrete examples of resins which can be used, of the MQ, MDQ, TD and MDT resins.

10 Preferably, mention may be made, as examples of resins which can be used, of the resins POS **B** functionalized by R^{fo} not comprising a Q unit in their structure. More preferably, mention may be made, as examples of resins which can be used, of the
15 functionalized TD and MDT resins comprising at least 20% by weight of T units and having a content by weight of group R^{fo} ranging from 0.3 to 5%. More preferably still, use is made of resins of this type in the structure of which at least 80% by number of the
20 substituents R^1 are methyl radicals. The functional groups R^{fo} of the resins **B** can be carried by the M, D and/or T units.

As regards the functionalized POSs **A** and the crosslinking agents **C**, mention may be made, as concrete
25 examples of substituents R^2 which are particularly suitable, of the same radicals as those mentioned by name above for the substituents R^1 of the functionalized polymers **A**, of the precursor polymers **A'** and **A''** and of the nonfunctionalized and unreactive
30 polymers **F**.

As regards the constituent substituents R^3 , R^4 and R^5 of the functionalization radicals R^{fo} , mention will preferably be made of C_1 - C_4 alkyl radicals; the methyl, ethyl, propyl, isopropyl and n-butyl radicals prove to
35 be more especially appropriate.

As regards each symbol Y, it represents, as has already been indicated, an oxygen atom or a divalent hydrocarbon group. Mention will preferably be made, as divalent hydrocarbon groups, of the methylene,

ethylene, propylene or butylene groups; the ethylene group is more particularly preferred.

According to the "more preferred embodiment of the invention" already mentioned above, each symbol Y represents an oxygen atom and the functionalization radicals R^{fo} are of alkoxy type and, in this context, according to an even more preferred embodiment, they result from silane crosslinking agents **C** chosen from the group consisting of:

- 10 $Si(OCH_3)_4$
- $Si(OCH_2CH_3)_4$
- $Si(OCH_2CH_2CH_3)_4$
- $(CH_3O)_3SiCH_3$
- $(C_2H_5O)_3SiCH_3$
- 15 $(CH_3O)_3Si(CH=CH_2)$
- $(C_2H_5O)_3Si(CH=CH_2)$
- $(CH_3O)_3Si(CH_2-CH=CH_2)$
- $(CH_3O)_3Si[CH_2-(CH_3)C=CH_2]$
- $(C_2H_5O)_3Si(OCH_3)$
- 20 $Si(OCH_2-CH_2-OCH_3)_4$
- $CH_3Si(OCH_2-CH_2-OCH_3)_3$
- $(CH_2=CH)Si(OCH_2CH_2OCH_3)_3$
- $C_6H_5Si(OCH_3)_3$
- $C_6H_5Si(OCH_2-CH_2-OCH_3)_3$.

25 In practice, the silane crosslinking agents **C** carrying the functionalization radicals R^{fo} which are very especially well suited are: $Si(OC_2H_5)_4$, $CH_3Si(OCH_3)_3$, $CH_3Si(OC_2H_5)_3$, $(C_2H_5O)_3Si(OCH_3)$, $(CH_2=CH)Si(OCH_3)_3$ or $(CH_2=CH)Si(OC_2H_5)_3$.

30 According to a noteworthy characteristic of the invention, the composition can additionally comprise at least one functionalization catalyst **D**, in the presence of which the reaction of the precursors **A'** and **A''** (and optionally of the precursors **B'** and **B''**) with the appropriate silane carrying the functional groups R^{fo} takes place, which reaction results in the POS **A** and in the resin **B** respectively.

In the case where the symbol Y represents an oxygen atom and where a condensation reaction of the

hydroxylated precursors **A'** and optionally **B'** with the silane **C** occurs, this functionalization catalyst **D** can advantageously be selected from the following compounds:

- 5 - potassium acetate (cf. US-A-3 504 051),
- various inorganic oxides (cf. FR-A-1 495 011),
- carbamates (cf. EP-A-0 210 402),
- lithium hydroxide (cf. EP-A-0 367 696),
- sodium hydroxide or potassium hydroxide (cf. EP-A-
- 10 0 457 693).

In some cases, it may be necessary to neutralize the functionalization catalyst. Thus, as regards lithium hydroxide, numerous products may be employed for this purpose, such as, for example:

- 15 - trichloroethyl phosphate,
- dimethylvinylsilyl acetate,
- a silyl phosphate of the type of those described in French patent FR-B-2 410 004,
- or a precipitated or fumed silica.

20 It is recommended, in the context of the present invention where the symbol Y represents an oxygen atom, to use lithium hydroxide, of formula LiOH or LiOH·H₂O, as functionalization catalyst **D**. It can be used, for example, in solution in at least one aliphatic alcohol

25 **E** having from 1 to 3 carbon atoms, such as, for example, methanol, ethanol or isopropanol, or a mixture of these alcohols. When one (or more) alcohol(s) is (are) present in the reaction medium, the amount employed lies within the range extending from 0.1 to 2

30 parts by weight and preferably from 0.2 to 1 part by weight, per 100 parts of hydroxylated polymer(s) **A'**.

Use is made of an effective amount of functionalization catalyst **D**, that is to say an amount such that the functionalization reaction rate is as

35 high as possible, in particular using Si(OC₂H₅)₄, CH₃Si(OCH₃)₃, CH₃Si(OC₂H₅)₃, (C₂H₅O)₃Si(OCH₃), (CH₂=CH)Si(OCH₃)₃ or (CH₂=CH)Si(OC₂H₅)₃ as functionalization agent, which is none other than the crosslinking agent **C**. In the majority of cases, use is

made of 0.001 to 5 mol of catalyst **D** per 1 mol of silanol groups ($\equiv\text{Si-OH}$) contributed, on the one hand, by the precursor(s) **A'** of the functionalized polymer(s) **A** and, on the other hand, by the precursor(s) **B'** of the functionalized resin(s) **B**. In the preferred case involving lithium hydroxide, use is made of 0.005 to 0.5 mol of LiOH per 1 mol of silanol groups of **A'** or **B'**.

The filler **G** provided is inorganic and can be composed of products chosen from siliceous or nonsiliceous materials.

As regards the siliceous materials, they can act as reinforcing or semireinforcing filler.

The reinforcing siliceous fillers are chosen from colloidal silicas, pyrogenic (or fumed) and precipitated silica powders, or their mixture.

These powders exhibit a mean particle size generally of less than 0.1 μm and a BET specific surface of greater than 50 m^2/g , preferably of between 100 and 350 m^2/g .

Semireinforcing siliceous fillers, such as amorphous silicas, diatomaceous earths or ground quartz, can also be employed.

As regards the nonsiliceous inorganic materials, they can be involved as semireinforcing or bulking inorganic filler. Examples of these nonsiliceous fillers, which can be used alone or as a mixture, are carbon black, titanium dioxide, aluminum oxide, alumina hydrate, expanded vermiculite, unexpanded vermiculite, calcium carbonate, zinc oxide, mica, talc, iron oxide, barium sulfate and slaked lime. These fillers have a particle size generally of between 0.001 and 300 μm and a BET specific surface of less than 100 m^2/g .

In practice but without implied limitation, the filler employed is pyrogenic silica powder; this silica is in the amorphous form when the aim is to obtain translucent mastics.

These fillers can be modified at the surface by treatment with the various organosilicon compounds

commonly employed for this use. Thus, these organo-silicon compounds can be organochlorosilanes, diorganocyclopolysiloxanes, hexaorganodisiloxanes, hexaorganodisilazanes or diorganocyclopolysilazanes (patents
5 FR 1 126 884, FR 1 136 885, FR 1 236 505 and GB 1 024 234). The treated fillers include, in the majority of cases, from 3 to 30% of their weight of organosilicon compounds.

The purpose of the introduction of the fillers is
10 to confer good mechanical and rheological characteristics on the elastomers resulting from the curing of the compositions in accordance with the invention. A single type of filler or mixtures of several types can be introduced.

15 As regards the curing catalyst I, mention may be made, as examples of symbols R^7 in the organic derivatives II.1 of formula (V), of the methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, hexyl, 2-ethylhexyl, octyl, decyl and dodecyl
20 radicals and, as examples of symbols L in the derivatives II.1 of formula (V), of the acetylacetonate ligand.

Mention may be made, as concrete examples of monomers II.1 of formula (V), of ethyl titanate or
25 zirconate, propyl titanate or zirconate, isopropyl titanate or zirconate, butyl titanate or zirconate, 2-ethylhexyl titanate or zirconate, octyl titanate or zirconate, decyl titanate or zirconate, dodecyl titanate or zirconate, β -methoxyethyl titanate or
30 zirconate, β -ethoxyethyl titanate or zirconate, β -propoxyethyl titanate or zirconate, the titanate or the zirconate of formula $M1[(OCH_2CH_2)_2OCH_3]_4$, bis(acetoacetyl)diisopropyl titanate or zirconate, or bis(acetoacetyl)dibutyl titanate or zirconate. The
35 monomeric metal compounds II.1 more particularly valued are the following products, taken alone or as a mixture: ethyl titanate, propyl titanate, isopropyl titanate or butyl (n-butyl) titanate.

Mention may be made, as concrete examples of

polymers **I1.2** originating from the partial hydrolysis of the monomers **I1.1**, of the polymers **I1.2** originating from the partial hydrolysis of isopropyl, butyl or 2-ethylhexyl titanates or zirconates.

5 Mention may be made, as also regards the curing catalyst **I**, as examples of symbols R^8 and R^9 in the derivatives **I2.1** and **I2.2** of formulae (VI) and (VII), of the propyl, isopropyl, butyl (n-butyl), isobutyl, sec-butyl, tert-butyl, hexyl, 2-ethylhexyl, octyl,
10 decyl and dodecyl radicals and, as examples of symbols **L** in the derivatives **I2.2** of formula (VII), of the acetylacetonate ligand.

 Mention may be made, as concrete examples of organic derivatives **I2**, of zinc dioctoate, tributyl
15 borate, bismuth carboxylate and aluminum acetylacetonate. The compounds **I2** more particularly valued are the following products, taken alone or as a mixture: zinc dioctoate, aluminum acetylacetonate or aluminum butoxide (linear or branched).

20 The respective amounts of each constituent **I1** or **I2** of the curing catalyst **I** can vary within wide limits, provided that they meet the abovementioned conditions (β) and (γ). These amounts are chosen according to the level of value desired as regards in
25 particular skin formation time, persistence of a tacky feel, hardness and initial hardness/final hardness ratio. An excellent compromise in values for its usage properties is obtained using an amount of curing catalyst **I** such that:

- 30 • (β) the number of $\mu\text{g.at}$ (microgram atoms) of the metals $M1 + M2$ introduced into 1 g of single-component composition comprising all the ingredients (i) to (8i) lies within the range extending from 25 to 55;
35 • (γ) the ratio:

$$\frac{\text{number of } \mu\text{g.at of } M2}{\text{total number of } \mu\text{g.at of } M1 + M2} \times 100$$

lies within the range extending from 10 to

45%.

According to another preferred embodiment of the invention, the single-component POS composition comprises:

- 5 - 100 parts by weight of linear diorganopolysiloxane(s) **A** functionalized by R^{fo} ,
- 0 to 30, preferably 5 to 15, parts by weight of resin(s) **B**,
- 0 to 15, preferably 3.5 to 7, parts by weight of crosslinking agent(s) **C**,
- 10 - 0 to 2, preferably 0 to 1, parts by weight of alcohol(s) **E**,
- 0 to 30, preferably 5 to 20, parts by weight of nonfunctionalized and unreactive linear diorganopolysiloxane(s) **F**,
- 15 - 2 to 40, preferably 8 to 20, parts by weight of inorganic filler **G**,
- 0 to 20 parts by weight of auxiliary agent(s) **H**, and
- an amount of curing catalyst **I** determined so as to contribute, to the composition, levels of metals M1 + M2 which meet the general or preferred conditions (β) and (γ) mentioned above.
- 20

The compositions in accordance with the invention cure at ambient temperature and in particular at temperatures of between 5 and 35°C in the presence of moisture. The curing (or the crosslinking) takes place from the exterior toward the interior of the body of the compositions. A skin is first formed at the surface and then the crosslinking continues in the body.

30 These compositions can be employed for multiple applications, such as pointing in the construction industry or the assembling and adhesive bonding of the most diverse materials (metals; plastics, such as, for example, PVC or PMMA; natural and synthetic rubbers; wood; board; earthenware; brick; glass; stone; concrete; masonry components), both in the context of the construction industry and in that of the automobile, domestic electrical appliance and electronics industries.

According to another of its aspects, another subject matter of the present invention (second subject matter of the invention) is a nonyellowing elastomer capable of adhering to various substrates and obtained
5 by crosslinking and curing the single-component silicone mastic composition described above.

The single-component organopolysiloxane compositions in accordance with the present invention are prepared with the exclusion of moisture, the
10 preparations being carried out in a closed reactor equipped with a stirrer in which it is possible, if need be, to apply vacuum and then optionally to replace the air expelled with an anhydrous gas, for example with nitrogen.

15 For this preparation, it is recommended to use equipment, operating batchwise or continuously, which makes it possible:

- to intimately mix, with the exclusion of moisture:
 - + in a stage 1, the following constituents:
20 precursor POS **A'** or **A''** of the POS **A** functionalized by R^{fo} , precursor resin **B'** or **B''** (optional) of the resin POS **B** functionalized by R^{fo} , silane, optionally olefinic, carrying the functional groups R^{fo}
25 R^{fo} (which can be the silane **C**), functionalization catalyst **D**, alcohol **E** (optional) and nonfunctionalized and unreactive POS **F** (optional);
 - + then, in a stage 2, the reaction mixture
30 from stage 1 supplemented by the addition of the constituents **G**, **H** (optional), **F** (optional) and **I**; and
- to discharge the volatile materials present (polymers of low molecular weight, alcohol formed during the
35 functionalization reaction, alcohol **E** optionally used) at various points in the implementation of the process:
 - + during the abovementioned stage 1 and/or
 - + during the abovementioned stage 2 and/or

+ in a final stage 3.

Other possible orders of introduction of the constituents, of course, exist for the implementation of this preparation process; for example, the following
5 order of introduction could be used:

- + stage 1: **A'** + optionally **B'** + **C** + **D** + optionally **E** + optionally **F** + **G**, with discharge at this stage of the volatile materials;
- 10 + stage 2: **C** + optionally **H** + optionally **F** + **I**.

Mention may be made, as examples of equipment, of slow dispersers, paddle, propeller, arm or anchor mixers, planetary mixers, hook mixers, or single-screw
15 or multiple-screw extruders.

Each of the stages employed in this preparation is carried out at a temperature lying within the range extending from 10 to 110°C. Preferably, each of the stages is carried out at a temperature extending from
20 15 to 90°C.

Stage 1 is carried out for a period of time sufficient (for example, extending from 10 seconds to 10 minutes) to bring about a complete functionalization reaction or a functionalization reaction which is as
25 close as possible to the maximum degree of functionalization accessible under the operating conditions chosen.

Stage 2 is carried out for a period of time sufficient (for example, extending from 10 seconds to
30 30 minutes) to arrive at homogeneous compositions.

Stage 3 is generally carried out under a reduced pressure of between 20×10^2 Pa and 900×10^2 Pa, for a period of time sufficient (for example, extending from 10 seconds to 1 hour) to discharge all the volatile
35 materials.

The invention will be better understood with the help of the following examples, which describe the preparation of neutral single-component compositions of alkoxy type which result in crosslinked elastomers

having or not having good usage properties, depending on whether or not they correspond to the present invention.

5 EXAMPLES 1 TO 15

1) Preparation of a single-component organopolysiloxane composition not including a curing catalyst (paste):

10 1030 g of α,ω -dihydroxylated polydimethylsiloxane oil with a viscosity of approximately 50 000 mPa.s and 33.0 g of crosslinking agent of vinyltrimethoxysilane type are charged to the vessel of a "butterfly" uniaxial mixer. The combined product is mixed at
15 200 rev/min for 2 min and 4.2 g of a lithium hydroxide functionalization catalyst are introduced into the vessel. The functionalization reaction is allowed to take place for 4 min with stirring at 400 rev/min and then 33.0 g of pyrogenic silica with a specific surface
20 of approximately 150 m²/g are incorporated at a moderate stirring rate (160 rev/min) and then at a higher stirring rate (4 min at 400 rev/min) to complete the dispersing thereof in the mixture. A rather thick but still flowing viscoelastic fluid is obtained. The
25 paste thus obtained is degassed under vacuum (6 min at 130 rev/min under a vacuum of 30×10^2 Pa) and then transferred into a container for storage.

2) Addition of the curing catalyst to the paste:

30

In order to obtain a mastic which crosslinks with atmospheric moisture, it is necessary to add a curing catalyst to the paste obtained above.

For the purpose of comparing different catalysts,
35 a predetermined amount of catalyst, the value of which is given in tables 1 to 4, which appear below, was added, in each example or test, to 30 g of paste.

The different catalysts, tested alone or in combination, are:

- tetrabutyl titanate (TBOT, from DuPont de Nemours);

- zinc dioctoate, formulated at 80% by weight in a mineral oil, comprising 18% by weight of zinc metal (DOZ, sold by Strem);

- aluminum acetylacetonate (ACAC/AL, sold by Strem);

- tributyl borate (TBB, sold by Strem);

- bismuth carboxylate, comprising 25% by weight of elemental bismuth (K-KAT 348, sold by King Industry).

3) Results:

The catalytic potentialities of each composition were evaluated in two ways:

- the skin formation time "SFT" (time at the end of which surface crosslinking is observed); the SFT is measured in the following way: a narrow strip of mastic is deposited and the surface of the narrow strip is, at regular time intervals, made flush with the end of a stick of wood. The skin formation time is determined by the time at the end of which mastic is no longer carried away when the stick is raised;

- the hardness (in Shore A) after crosslinking at 23°C/50% RH for 7 days (the hardness is measured on a disk-shaped specimen with a thickness of 6 mm obtained by the superimposition of 3 plaques each with a thickness of 2 mm, according to the instructions of the standard ASTM-D-2240).

3.1) TBOT-ACAC/AL cocatalysis (examples 1 to 4):

Table 1

Ex./Tests	[Al], in $\mu\text{g.at/g}$	[Ti], in $\mu\text{g.at/g}$	(β) in $\mu\text{g.at/g}$	(γ) in %	SFT, in hours	Hardness at 7 days (Shore A)
Ex. 1	3.8	3.8	7.6	50.0	2	13
Ex. 2	38	3.8	41.8	90.9	2	15.5
Ex. 3	3.8	38	41.8	9.1	0.33	19
Ex. 4	38	38	76	50.0	0.33	19
Test A	3.8	0	3.8	100.0	> 4	0
Test B	38	0	38	100.0	> 4	10
Test C	0	3.8	3.8	0.0	> 4	0
Test D	0	38	38	0.0	0.5	19

5

3.2) TBOT-DOZ cocatalysis (examples 5 to 8):

Table 2

Ex./Tests	[Zn], in $\mu\text{g.at/g}$	[Ti], in $\mu\text{g.at/g}$	(β) in $\mu\text{g.at/g}$	(γ) in %	SFT, in hours	Hardness at 7 days (Shore A)
Ex. 5	3.8	3.8	7.6	50.0	1.75	14
Ex. 6	38	3.8	41.8	90.9	1.5	18.5
Ex. 7	3.8	38	41.8	9.1	0.25	21
Ex. 8	38	38	76	50.0	0.25	17.5
Test E	3.8	0	3.8	100.0	> 4	0
Test F	38	0	38	100.0	> 4	0
Test C	0	3.8	3.8	0.0	> 4	0
Test D	0	38	38	0.0	0.5	19

3.3) TBOT-TBB cocatalysis (examples 9 to 12):

Table 3

Ex./Tests	[B], in μg.at/g	[Ti], in μg.at/g	(β) in μg.at/g	(γ) in %	SFT, in hours	Hardness at 7 days (Shore A)
Ex. 9	3.8	3.8	7.6	50.0	2	0
Ex. 10	38	3.8	41.8	90.9	2	2
Ex. 11	3.8	38	41.8	9.1	0.375	20
Ex. 12	38	38	76	50.0	0.25	20
Test G	3.8	0	3.8	100.0	> 4	0
Test H	38	0	38	100.0	2	0
Test C	0	3.8	3.8	0.0	> 4	0
Test D	0	38	38	0.0	0.5	19

5

3.4) TBOT-K-KAT cocatalysis (examples 13 to 15):

Table 4

Ex./Tests	[Bi], in μg.at/g	[Ti], in μg.at/g	(β) in μg.at/g	(γ) in %	SFT, in hours	Hardness at 7 days (Shore A)
Ex. 13	6	3.8	9.8	61.2	2	12.5
Ex. 14	24	3.8	27.8	86.3	1.75	2
Ex. 15	6	38	44	13.6	0.33	20
Test I	6	0	6	100.0	> 4	3
Test J	24	0	24	100.0	> 4	7.5
Test C	0	3.8	3.8	0.0	> 4	0
Test D	0	38	38	0.0	0.5	19

10

3.4) Comments:

The data demonstrating a synergistic effect are mentioned in bold in tables 1 to 4 above.

15

In these tables, it is noticed that there is systematically a concerted action between the catalysts which results in an overall improvement in the cross-

linking kinetics. If, for example, DOZ is taken (table 2), it is noticed that the introduction of the combination according to the invention comprising 3.8 $\mu\text{g.at/g}$ (microgram atoms of zinc metal per gram of catalyst-free single-component composition) of DOZ and 3.8 $\mu\text{g.at/g}$ of TBOT results in a reduction in the SFT (which changes to 1.75 hours) and in particular in an acceleration in the crosslinking kinetics for the elastomer, resulting in a Shore A hardness of 14 after 7 days, whereas the use of 3.8 $\mu\text{g.at/g}$ of DOZ or of TBOT, taken alone, results in an SFT of greater than 4 h and a zero hardness after 7 days.

The most advantageous synergies are contributed by the Ti-Al and Ti-Zn cocatalyses.

EXAMPLES 16 TO 21

1) Preparation of single-component organopolysiloxane compositions comprising, as curing catalyst, different amounts of the DOZ + TBOT catalytic combination:

704 g of α,ω -dihydroxylated polydimethylsiloxane oil with a viscosity of approximately 135 000 mPa.s, 48 g of α,ω -trimethylsilylated polydimethylsiloxane oil with a viscosity of approximately 100 000 mPa.s, 180 g of α,ω -trimethylsilylated polydimethylsiloxane oil with a viscosity of approximately 100 mPa.s, 79 g of a hydroxylated silicone resin (this resin, of MDT type and having 1% by weight of hydroxyl radicals, is composed of 4% by weight of $(\text{CH}_3)_3\text{SiO}_{1/2}$ units, 71% by weight of $(\text{CH}_3)_2\text{SiO}_{2/2}$ units and 25% by weight of $\text{CH}_3\text{SiO}_{3/2}$ units; this resin exhibits a viscosity of 100 mPa.s at 25°C) and 36 g of crosslinking agent of vinyltrimethoxysilane type are charged to the vessel of a "butterfly" uniaxial mixer. The combined product is mixed at 200 rev/min for 2 min and 4.6 g of a lithium hydroxide functionalization catalyst are introduced into the vessel. The functionalization reaction is allowed to take place for 4 min with stirring at

400 rev/min and then 114 g of amorphous silica, sold by Degussa under the name R104, are incorporated at a moderate stirring rate (160 rev/min) and then at a higher stirring rate (4 min at 400 rev/min) to bring to completion the dispersing thereof in the mixture. 18 g of methacryloyloxypropyltrimethoxysilane (MEMO) are then added and the curing catalyst formed by the combination of DOZ and TBOT is subsequently introduced according to the amounts which appear in table 4 given below. After mixing at 400 rev/min for 4 min, the stirring rate is reduced to 130 rev/min and the mixture is degassed under vacuum at 20×10^2 Pa.

2) Results:

15

Two criteria were monitored:

- the tacky feel after crosslinking at 23°C under 50% relative humidity for 17 hours (three different experimenters were asked to categorize the 4 mastics according to the persistence of the tacky feel); this test consists in causing a roller to run down over the film of crosslinked mastic; the film is deposited on an inclined plane, the slope of which can be varied; the time (in seconds) at the end of which the roller has run down the entire slope is recorded; the slope is varied from 10° to 40°; the results obtained for the slopes of 30° to 40° are very similar and it is not possible to differentiate them.

30

- the ratio (expressed in %) of the hardness (in Shore A) at 24 hours to the hardness at 7 days (the hardness is measured on a disk-shaped specimen with a thickness of 6 mm obtained by the superimposition of 3 plaques each with a thickness of 2 mm, according to the instructions of the standard ASTM-D-2240); a ratio of 100% means that the maximum of the hardness value was achieved after crosslinking for 24 hours.

35

Table 5

Examples	TBOT: [Ti], in μg.at/g	DOZ: [Zn], in μg.at/g	(β) in μg.at/g	(γ) in %	Measurement of the tacky feel (10° slope) in s	Ratio of the hardnesses, %
Ex. 16	23.55	16.79	40.34	42	13.4	100
Ex. 17	33.14	16.79	49.93	34	9.4	100
Ex. 18	18.89	10.46	29.35	36	9.7	89
Ex. 19	28.49	10.46	38.95	27	12.9	85
Ex. 20	37.79	10.46	48.25	22	11.7	81
Ex. 21	33.14	3.85	36.99	10	11.7	76
Ex. 22	23.55	3.85	27.40	14	16.7	71
Test K	37.79	0.00	37.79	0	35.9	70

Comments:

5 The effects of synergy between the two compounds are slightly different according to whether the tacky feel or the hardness ratio is considered.

10 As regards the tacky feel, the effect is noteworthy from a very low level of zinc (10%), as is shown by the comparison of example 21 with test K.

15 As regards the ratio of the hardnesses, the above table allows it to be observed that it changes virtually continuously with the [Zn]/Total ratio with a ratio of 100% reached from a level of Zn of 34%, this being the case without a significant increase in the total amount of catalyst, as is illustrated in example 16. The advantage can be evaluated in this case at an improvement of 50% in the setting kinetics of the silicone elastomer.

20 It should be noted that, in example 16, the amount of TBOT is reduced by almost 40% with respect to the reference test K and that the setting rate is improved at the same time.